

PROJECT NUMBER: 2500
PROJECT TITLE: Fundamental Chemistry
PROJECT LEADER: J. I. Seeman
PERIOD COVERED: October, 1987

I. FLAVOR/ODOR CHEMISTRY (Paine, Secor, Seeman)

- A. **Objective:** To develop new technologies for smoke deliveries of desired flavorants; to prepare new substances for flavor/odor evaluation; to develop methodologies for the analysis of subjective data; to derive relationships between physicochemical parameters and subjectives.
- B. **Results and Plans:** Excellent progress is being made toward the synthesis of large quantities of all seven configurational stereoisomers of menthol. Pure (99.3+%) samples of d-Neoisomenthol and d-Neomenthol, were prepared and submitted for evaluation by the Odor Profiling Panel and, along with recrystallized d-isomenthol, to Flavor Development. A large scale preparation of pure d-menthol from di-d-menthyl 2,6-naphthalene dicarboxylate was effected, preparatory to oxidation to d-menthone. To improve the equilibrium content of d-isomenthone, l-menthone was epimerized (over K_2CO_3) at its boiling point, as a model reaction. The d-isomenthone content (reportedly 29% at room temperature), was increased to 37%.

As the first step in enhancing our patent position on the flavor release of substituted heterocycles in addition to pyridines and pyrazines, two trimethylisoxazole release agents were prepared. Initial pyrolysis studies are in progress. In addition, the two anethole release agents whose smoke chemistry (SS/MS) was recently characterized by S. Tafur and B. Levins are being examined by competitive pyrolysis.

II. APPLICATIONS OF THEORETICAL CHEMISTRY (Kao, Seeman)

- A. **Objective:** Develop the necessary algorithms and software to study physical properties of flavor and tobacco related molecules; utilize these techniques to model tobacco smoke and pyrolysis chemistry.
- B. **Results and Plans:** Efforts have been in extending the MOMM approach to nitrogen-containing compounds. Successful progress has been made in expanding the MOMM method to C-nitroso compounds and nitrites. Ab initio calculations of models for C-nitroso compounds and nitrites are near completion.

We have initiated theoretical mechanistic studies of the glycerol-acrolein reaction. Semi-empirical calculations of the ground-state structures and energies for model compounds were completed. Efforts are now concentrated in locating relevant transition-state geometries. Catalytic effects such as $Mg(OH)_2$, on ground and transition states will be investigated.

MNDO molecular orbital theory has been systematically employed to investigate the pyrolysis mechanisms of β -hydroxypropanal, β -hydroxypropionic acid, and β -hydroxypropionate. These serve as models for various flavor release systems.

A pseudo cyclic 6-membered transition state is confirmed in all three cases. MNDO results provide the adequate data for further refinement and higher level of studies. A complete report has been issued.

MOMM calculations were performed on a variety of alkyl substituted benzenes which are being studied with E. R. Bernstein.

III. CHEMICAL PHYSICS STUDIES OF TOBACCO CONSTITUENTS (Secor, Seeman)

- A. Objective: To obtain structural information about important tobacco constituents/flavorants; to develop information on cluster and aerosol formation and chemistry.
- B. Results and Plans: The supersonic molecular jet spectroscopy (SMJS) study of alkylbenzenes is essentially complete. Anethole and related styrenes are being investigated, and preliminary experiments have been started to determine if chemical reactions in clusters can be observed for the first time. The reaction of anethole with water has been investigated and preliminary results are very interesting.

A number of substrates for examination by SMJS have been prepared, namely 4-dimethylaminobenzotrifluoride and 4-di-trideuteromethyl-aminobenzonitrile.

IV. MISCELLANEOUS (Leister, Secor)

- A. Objective: To convert important programs of the Chemical Research Division from the DEC system to the UNIX system.
- B. Results: A log of current users of the DEC system for this Division was obtained from CAD and work has begun in converting the remaining programs and files to the UNIX system.

A total of twelve synthetic samples, mostly tobacco alkaloids, were given to various PM researchers in support of their work.

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